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Stress Relaxation of Ramie Fiber during Acid Hydrolysis

Tsutomu AOKI* and Tadashi YAMADA*

Abstract—Stress relaxation measurements for ramie fiber were carried out during hydrolysis with sulfuric acid. The mechanism of stress decay was discussed, and an attempt was made to separate physical and chemical relaxation mechanisms. The results obtained were as follows:

(1) The relative stress $f(t)/f(1)$ for ramie fiber during hydrolysis could be represented by the following equation:

$$f(t)/f(1) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$$

where A_1 is a constant and τ_1 is the relaxation time ($\tau_1 < \tau_2$). It was considered that the first term in the above equation represents the stress decay behavior due to scission of hydrogen bonds in the amorphous region of cellulose, while the second term represents the chemical relaxation due to the scission of glucosidic bonds.

(2) The apparent activation energies for the two relaxation processes were 16 kcal/mole (physical relaxation process) and 12 kcal/mole (chemical relaxation process). The activation energy of chemical relaxation was close to that obtained from diffusion controlled reaction.

(3) It may be concluded that the value of A_1 in the above equation represents the fraction of bonds such as hydrogen bonds which contribute to the physical relaxation process.

(4) The relaxation time τ_2 of chemical relaxation was nearly equal to the inverse of the rate constant, $1/k$, obtained from measurements of the degree of polymerization.

Introduction

If, in a suitable apparatus, reagents that influence the rate of stress relaxation are added to materials under load, it is sometimes possible to analyze the data obtained in terms of physical and chemical processes. By employing the technique of stress relaxation of cellulose fibers immersed in an attacking reagent, LEMISZKA *et al.*¹⁾ determined the relative accessibility of fibers and CANTER²⁾ proposed a theoretical equation valid for chemical stress relaxation of all materials containing a fine-grained, ordered distribution. However, the mechanism of stress relaxation was considered only very briefly.

The chemical relaxation of wood seems to be remarkably affected by the scission of β -1, 4 glucosidic bonds in holocellulose which is the main constituent of wood, because these glucosidic bonds are easily broken by the addition of an acid catalyst³⁾. Therefore, we have studied the chemical stress relaxation of wood during acid hydrolysis^{4~7)}. Since, however, wood is a composite material consisting of such diverse materials as cellulose, hemicellulose and lignin, it is very difficult to analyze the data

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obtained from stress relaxation measurements of wood during hydrolysis. This paper, using ramie fiber which consists mainly of cellulose, describes an attempt to separate physical and chemical relaxation mechanisms.

Experimental

Refined ramie fiber was used as supplied by Nihon Seni Koogyo Co., Ltd.. The fiber samples were extracted with ether. Stress relaxation measurements of ramie fibers were performed by a balance-chain-type relaxometer at temperatures of 25, 35, 45, 55 and 60°C in 0, 1, 5 and 10% sulfuric acid. A schematic diagram of the relaxometer is shown in Fig. 1. The dimensions of the fibers are either about 3 cm or about 5 cm long depending on the type of test and 0.0013 to 0.0015 cm in diameter. Their diameter was determined by micrometer.

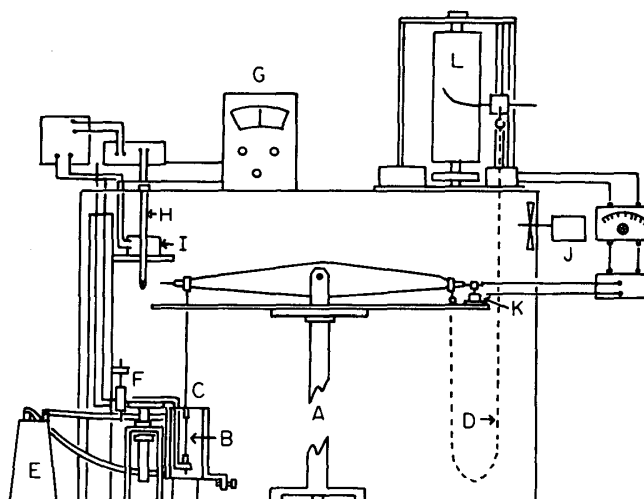


Fig. 1. Schematic diagram of relaxometer. A: balance, B: specimen, C: reaction cell, D: chain, E: circulator (hot water), F: differential transformer, G: displacement meter, H: thermostat, I: heater, J: fan, K: point of contact, L: recorder.

The stress relaxation measurements were carried out as follows. The sample fiber was fixed between the clamps and was kept in distilled water in a slack state for about 30 minutes at the desired temperature before being extended. The fiber was then stretched quickly to a predetermined, constant elongation and stress decay was observed. The chemical stress relaxation measurements were carried out in two ways. The sample was either immersed in sulfuric acid from the beginning, or stress relaxation was observed in distilled water for about 500 minutes at which time the rate of relaxation had become very small, and then the water was removed and the sample was immersed in sulfuric acid.

Results and Discussion

1) Separation of physical and chemical relaxations

Fig. 2 illustrates the relative stress $f(t)/f(1)$ (force at time t normalized to the force at one minute after the start of extension) as a function of time for ramie fiber during hydrolysis with 10% sulfuric acid at various temperatures. Although in the semi-logarithmic scale the relative stress decreases almost linearly with $\log t$ at the shorter time region, with increasing time the departure from linearity becomes more pronounced and the relative stress decreases rapidly. With increasing temperature this rapid decay of relative stress starts earlier. On the other hand, when the same data are plotted on a $\log f(t)/f(1) - t$ scale as shown in Fig. 3, relative stress decreases linearly with increasing time at the longer time region.

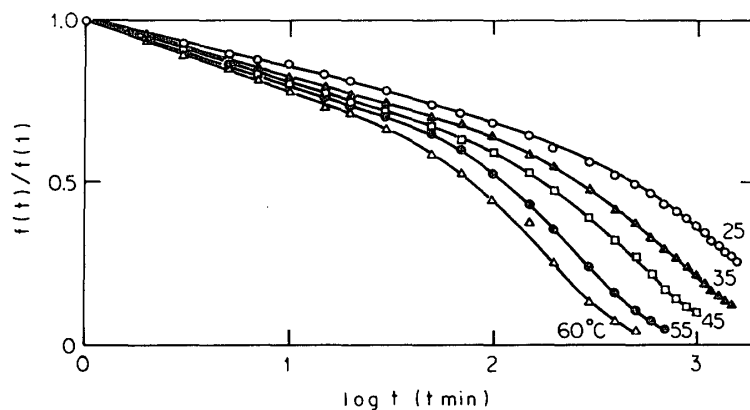


Fig. 2. Stress relaxation curves for ramie fiber during hydrolysis with 10% sulfuric acid at various temperatures.

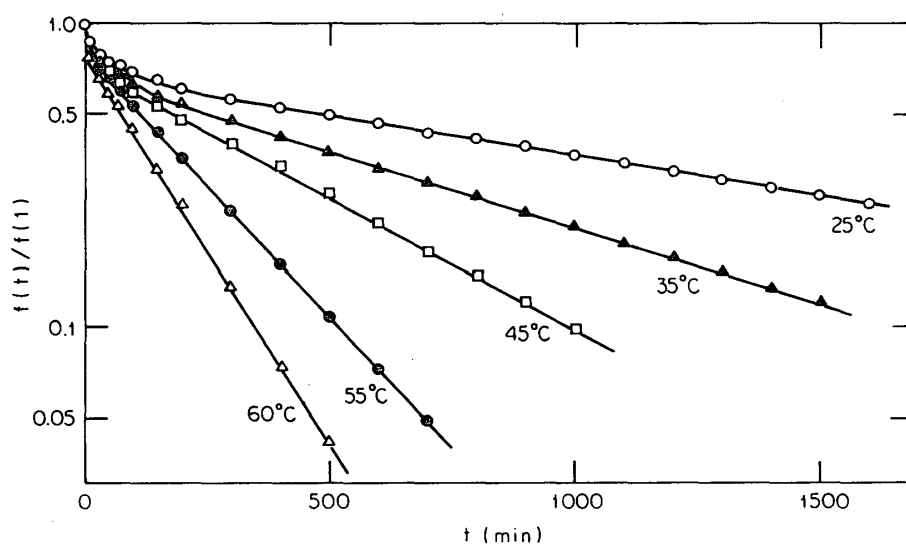


Fig. 3. Stress relaxation curves for ramie fiber during hydrolysis with 10% sulfuric acid at various temperatures.

The cleavage of primary bonds in cellulose is responsible for the stress decay at small, constant extension while immersed in acid such as hydrochloric acid and sulfuric acid, and the following equation is used empirically to describe the process of stress decay.⁸⁾

$$f(t)/f(0) = \sum_{n=1}^{\infty} A_n \exp(-k_n t) \quad (1)$$

where $f(t)$ is the stress at time t , $f(0)$ is the initial stress, and A_n and k_n are constants. CANTER²⁾ assumed that the structure of cellulose microfibrils can be approximated by a distribution of ordered regions, ranging in degree of order n from the totally amorphous to the completely crystalline, and considered that the stress decay of such systems held at small, constant extension, while immersed in a medium containing a reactive reagent, is given a MARKOV statistical development. He indicated theoretically that equation (1) could be used to describe the data obtained from such an experiment at a particular temperature and acid concentration.

When the stress relaxation curves for ramie fiber during hydrolysis in Fig. 3 are analyzed by using an extrapolation procedure known as TOBOLSKY's Procedure X⁹⁾ which resolves a particular k_n and its conjugate A_n from the experimental data, the process of stress decay can be represented by the following equation which corresponds to the equation for two MAXWELL models.

$$f(t)/f(1) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) \quad (2)$$

The values of the coefficients A_1 , A_2 and the relaxation times τ_1 , τ_2 are given in Table 1. The value of A_1 decreased with increasing temperature.

Table 1. Relaxation coefficients for ramie fiber during hydrolysis with sulfuric acid.

Temperature (°C)	Concentration (%)	τ_1 (min.)	A_1	τ_2 (min.)	A_2
25	10	90	0.324	1560	0.676
35		53	0.322	850	0.678
45		25	0.282	500	0.718
55		6.2	0.209	250	0.791
60		5.0	0.211	180	0.789

The stress decay behavior in the shorter time region may be considered to correspond to the first term in equation (2). The relative stress in this region is non-linear as shown in Fig. 3. In the chemical relaxation of butadiene rubbers¹⁰⁾, it is considered that physical relaxation occurs in this non-linear region. In plotting the slope of the stress relaxation curve at a given time as a function of temperature, wet Hinoki as well as ramie fiber gave well defined maxima in the plot¹¹⁾. From these previous results it was concluded that relaxation in this region took place principally by scission of hydrogen bonds in the amorphous region of cellulose.

On the other hand, the second term in equation (2) represents the chemical relaxation which is caused by the reaction between acid and cellulose, and it is considered that the process is due to the scission of glucosidic bonds. LEMISZKA *et al.*¹³ reported that the drastic reduction in stress of cellulose fibers following addition of 0.1 N hydrochloric acid at 30°C is caused presumably by the rupture of primary bonds such as glucosidic bonds and not the breaking of secondary linkages.

2) *Activation energies of both relaxation processes*

The apparent activation energies for the two relaxation processes obtained from the relaxation time τ_1 and τ_2 in Table 1 were 16 kcal/mole (physical relaxation process) and 12 kcal/mole (chemical relaxation process). Comparison of these values of physical relaxation with previously published values from purely physical experiments^{4,6}) showed good agreement for ramie fiber but slightly lower values for Hinoki. On the other hand, the activation energy of chemical relaxation was low in comparison with that due to the scission of glucosidic bonds obtained from measurements of either viscosity or weight loss under chemical reaction (about 30 kcal/mole). Therefore, it is considered that the activation energy of the chemical relaxation process in sulfuric acid solution for ramie fiber which was initially in the wet condition was close to that obtained from the heterogeneous reaction, mentioned previous paper⁴).

The activation energy of the diffusion process for Dinitrile A fiber was 14 kcal/mole¹³) using the chemical stress relaxation technique and the activation energy for keratin in diffusion controlled reaction was about 14 kcal/mole¹⁴). However, the activation energies obtained from chemical stress relaxation measurements are not always the same as those of diffusion controlled heterogeneous reactions. However, the apparent activation energy of Hinoki which was initially swollen in dimethyl sulfoxide was 28.5 kcal/mole and when subsequently treated with a mixture of diethyl amine, sulfur dioxide and dimethyl sulfoxide it was 34.7 kcal/mole⁶). These values were almost equivalent to those obtained from measurements of either viscosity or weight loss under homogeneous chemical reaction.

3) *Significance of the constant A*

Stress relaxation curves for ramie fiber immersed successively in distilled water and 10% sulfuric acid at 25°C are shown in Fig. 4(A). Following the addition of sulfuric acid, a drastic reduction in stress occurs which is more pronounced than that obtained in water alone. Fig. 4(B) shows similar data after addition of 1, 5 and 10% sulfuric acid, but only the relative stress after addition of acid is plotted. In the shorter time region there is virtually no effect of acid concentration. This is probably due to the fact that hydrogen bonds which contribute to physical relaxa-

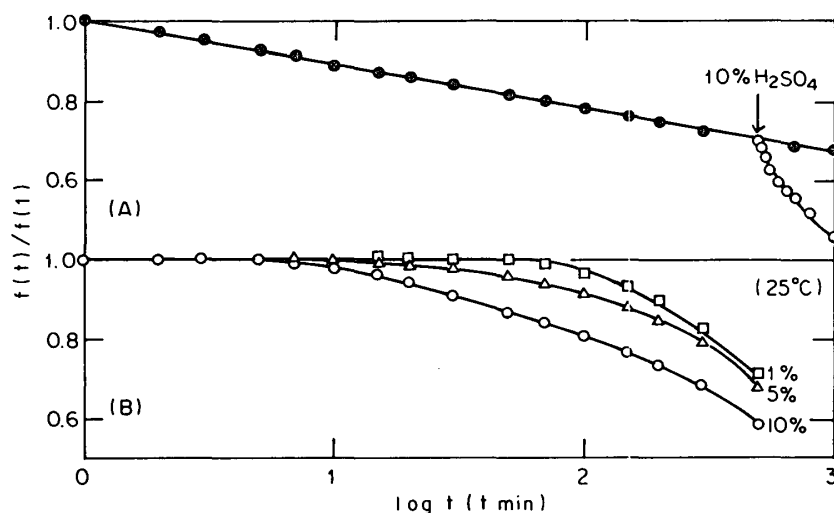


Fig. 4. (A) Stress relaxation data for ramie fiber at 25°C, first in distilled water and then in 10% sulfuric acid. (B) Data similar to those of (A) but omitting the portions of the stress relaxation curves prior to the addition of 1, 5 and 10% sulfuric acid at 25°C.

Table 2. Relaxation coefficients for ramie fiber during hydrolysis with sulfuric acid.

Temperature (°C)	Concentration (%)	τ_1 (min.)	A_1	τ_2 (min.)	A_2
25	1			1300	
	5	31	0.016	1340	0.984
	10	150	0.133	1270	0.867

tion were broken previously so that sulfuric acid diffusion has little or no effect. However, at longer times glucosidic bonds are broken by the sulfuric acid, and chemical relaxation occurs. Furthermore, this relaxation process occurs earlier as the acid concentration increases.

Table 2 shows the relaxation times τ_1 and τ_2 , and the constants A_1 and A_2 obtained from the data presented in Fig. 4. The value of A_1 is low compared with that obtained from data with immediate immersion in sulfuric acid. From these results, it may be concluded that the value of A_1 represents the fraction of bonds such as hydrogen bonds which contribute to the physical relaxation process. CANTER²⁰ reported that A_n in equation (1) is the fraction of bonds characteristic of the region with degree of order n .

4) Relaxation time and Rate Constant

Assuming that the breaking of one glucosidic bond would result in a definite increment of stress decay, the rate of stress relaxation corresponds to the reaction rate during hydrolysis. In order to investigate this correspondence, it is necessary to know the degree of polymerization as a function of time. SHARPLES^{15,16)} and

HIGGINS *et al.*¹⁷⁾ reported that the relationship between the degree of polymerization and reaction time can be represented approximately by the following equation at a certain temperature and sulfuric acid concentration:

$$2/\bar{P}_w(t) - 2/\bar{P}_w(0) = \alpha kt \quad (3)$$

where $\bar{P}_w(0)$ and $\bar{P}_w(t)$ are the weight average degrees of polymerization as determined by viscosity experiments at time 0 and time t , respectively, α is the fraction of glucosidic bonds available for hydrolysis and k is the rate constant for hydrolysis of cellulose. Since k varies with temperature and sulfuric acid concentration, it can be calculated by use of the following equations.

$$\ln \alpha_1 k_1 - \ln \alpha_2 k_2 = E_{act}/R \times (1/T_2 - 1/T_1) \quad (4)$$

$$\log \bar{P}_w(7200)/\bar{P}_w(0) = -1.356 \times 10^{-2} C \quad (5)$$

where E_{act} is activation energy (cal/mole), R is the Gas constant (1.987 cal/deg. mole), T is the absolute temperature ($^{\circ}K$) and C is the sulfuric acid concentration (weight percentage). Equation (5) which shows the relationship between sulfuric acid concentration and the degree of polymerization was obtained from the data of HIGGINS *et al.*¹⁷⁾

Fig. 5 shows the relative stress and the degree of polymerization as a function of time during hydrolysis with 10% sulfuric acid at various temperatures. The relative stress $f(t)/f(1)$ as a function of time is due to the chemical relaxation process which has been separated by use of equation (2) and the values of $(\bar{P}_w(t) - \bar{P}_w(\infty))/(\bar{P}_w(1) - \bar{P}_w(\infty))$ represent the degree of polymerization obtained from equations (3), (4) and (5), based on the data of SHARPLES¹⁶⁾ and HIGGINS *et al.*¹⁷⁾ Assuming that an

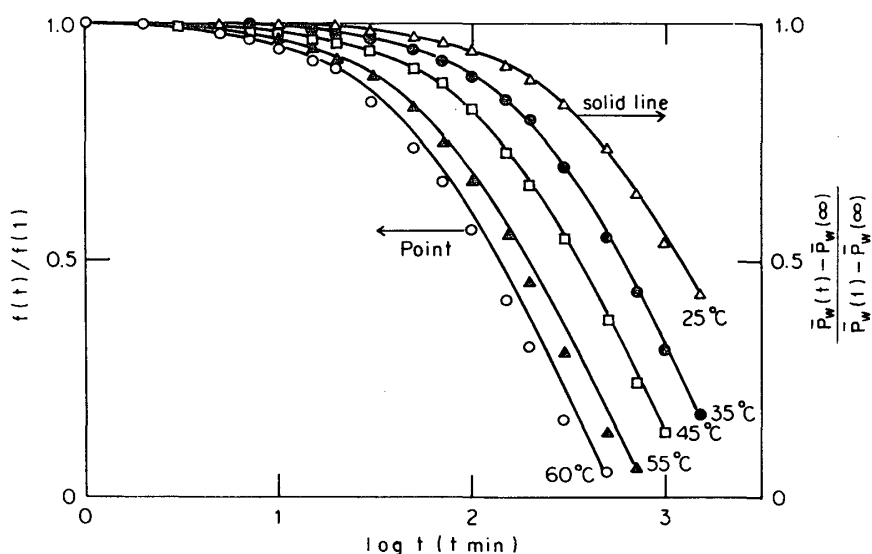


Fig. 5. Chemical stress relaxation $f(t)/f(1)$ for ramide fiber (points) and degree of polymerization $(\bar{P}_w(t) - \bar{P}_w(\infty))/(\bar{P}_w(1) - \bar{P}_w(\infty))$ obtained from equations (3), (4) and (5) (solid lines) during hydrolysis with 10% sulfuric acid at various temperatures.

equilibrium degree of polymerization $\bar{P}_w(\infty)$, exists at this experimental temperature and the acid concentration used⁷⁾, the value of relative degree of polymerization can be considered as being equal to the value of relative stress at the time of last measurement. The solid lines in Fig. 5 represent the degree of polymerization and the points represent the relative stress. The relative stress values are in good agreement with the values of the degree of polymerization at each temperature. The relaxation time τ_2 of chemical relaxation was nearly equal to the inverse of the rate constant, $1/k$, obtained from measurements of the degree of polymerization.

Conclusion

Since wood is a composite material consisting of such diverse materials as cellulose, hemicellulose and lignin, it is very difficult to analyze the data obtained from stress relaxation measurements during hydrolysis. However, using ramie fiber which consists mainly of cellulose, the data obtained can be analyzed in terms of physical and chemical processes.

This paper describes an attempt to separate physical and chemical relaxation mechanisms. It showed that the process of stress decay could be represented by an equation which corresponds to the equation for two MAXWELL models. Furthermore, it was considered that the MAXWELL models represented the stress decay behavior due to scission of hydrogen bonds in the amorphous region of cellulose, and the stress decay due to the scission of glucosidic bonds, respectively. If chemical relaxation occurs due to the scission of glucosidic bonds, the rate of relaxation will correspond to the reaction rate during hydrolysis. Assuming that the breaking of one glucosidic bond would result in a definite increment of stress decay, the relaxation time of chemical relaxation was nearly equal to the inverse of the rate constant obtained from measurements of the degree of polymerization.

Comparing the value of A_1 in equation (2) obtained from data with immediate immersion in sulfuric acid with that obtained from data of samples immersed successively in distilled water and sulfuric acid, it may be concluded that the value of A_1 represents the fraction of bonds, such as hydrogen bonds, which contribute to the physical relaxation process. On the other hand, the apparent activation energy of chemical relaxation for ramie fiber which was initially in the wet condition was close to that obtained from the diffusion controlled reaction. However, based on results obtained with wood, it is considered that the activation energy of the chemical relaxation for ramie fiber treated with dimethyl sulfoxide will be almost equivalent to those obtained from measurements of either viscosity or weight loss under homogeneous chemical reaction.

These results show that the chemical relaxation behavior of cellulosic materials

such as ramie fiber can be studied effectively if the measurements are carried out under condition where physical relaxation is either comparatively low or entirely absent. Further improvements are obtained if the reaction is facilitated by using swollen fibers treated with such reagents as dimethyl sulfoxide.

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